

1211193

NO DRAWINGS

- (21) Application No. 33636/66 (22) Filed 26 July 1966
 (21) Application No. 14209/67 (22) Filed 29 March 1967
 (23) Complete Specification filed 26 Oct. 1967
 (45) Complete Specification published 4 Nov. 1970
 (51) International Classification C 08 f 7/00
 (52) Index at acceptance
 C3P 13D5A 13D5X 13DX 13F3 13G2A 13G4A 13G5 13H3
 13T1X 13Y



(72) Inventors RAYMOND LLOYD WILLIAMS, DAVID HUGH RICHARDS and DAVID ANTHONY SALTER

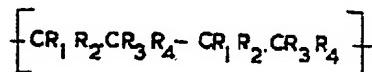
(54) POLYMERS OF UNSYMMETRICALLY SUBSTITUTED ALKENES

(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation established by Statute, of Kingsgate House, 66—74, Victoria Street, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

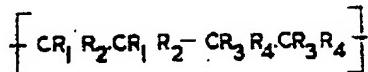
The invention relates to polymers of unsymmetrically substituted alkenes, especially vinyl compounds, and to processes for their manufacture.

The polymerisation of substituted alkenes generally, and in particular of vinyl compounds, is well known. Polymerisation of these monomers by normal methods e.g. free radical initiated polymerisation, might theoretically give three types of polymeric product for the generic substituted alkene $R_1R_2C=CR_3R_4$. These types could be.

1. Head-to-tail polymer:



2. Head-to-head and tail-to-tail:



3. A mixture of types 1 and 2.

In practice, polymerisation is found to take place to give head-to-tail polymers of type 1. It will be appreciated that these types of linkage between monomeric units in the polymer may only be distinguished when a substituent on, say the carbon atom carrying R_3 and R_4 (the "head" of the monomeric unit) is different from the substituents on the carbon atom carrying R_1 and R_2 (the "tail" of the monomeric unit). Such considerations thus can be applied only to substituted alkenes which are unsymmetrical about the alkenic bond and it is in this sense that the term "unsymmetrical" is used throughout the specification and claims.

In accordance with the present invention, however, there are provided novel polymers of unsymmetrical substituted alkenes in which the monomer units forming the polymer are bonded predominantly in the head-to-head and tail-to-tail configuration in contrast to the conventional head-to-tail bonded polymers. The novel polymers differ significantly in properties from the corresponding head-to-tail polymers, generally as a result of their differing steric structure, and this is reflected particularly in physical properties such as thermal stability and nuclear magnetic resonance spectra. Thus, for example, head-to-tail linked α -methylstyrene degrades at 284°C to yield more than 95% monomer, whereas the corresponding head-to-head linked polymer yields less than 1% monomer under the same conditions. Again, head-to-head linked poly(vinylchloride) has enhanced thermal stability as compared with the conventional

BEST AVAILABLE COPY

[Price 5s. Od. (25p)]

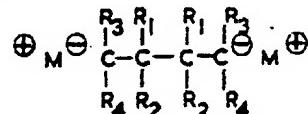
polymer and may be used advantageously in place of the conventional polymer in higher temperature environments. Head-to-head linked poly(vinylpyridine) possesses semi-conductor properties which may be useful in the electronics industry.

5 A further important use for head-to-head polymers in accordance with the invention is in the study of the thermodynamic and kinetic properties of bulk polymer systems. Conventional methods of studying these characteristics involve carrying out dilution experiments with solutions of the polymer being studied. While such methods are accurate for relatively small molecules, the size of large polymer molecules means that reaction rates are normally diffusion controlled. This rate of diffusion is affected by 10 dilution with conventional solvents and the accurate assessment of the polymer properties is prevented. It has now been found that kinetic data for conventional head-to-tail polymers may be obtained accurately by diluting them with the corresponding head-to-head polymer which is indistinguishable so far as diffusion rate is concerned, but which may be distinguished analytically to give accurate results for the head-to-tail 15 polymer being studied.

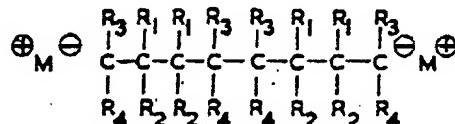
15 According to the invention polymers of unsymmetrical substituted alkenes having predominantly head-to-head and tail-to-tail linkages between monomer units may be prepared by a process which broadly comprises reacting an electron transfer agent, M or M^+A^- where M is an alkali or an alkaline earth metal and A⁻ is an anion derived from a polynuclear aromatic hydrocarbon (that is a hydrocarbon having at least 20 two aromatic rings) compound, with a monomer having the formula:



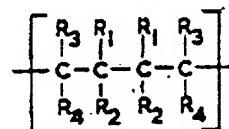
wherein R₁, R₂, R₃ and R₄ are hydrogen, or halogen, or a univalent radical chosen 25 from alkyl, aryl, aralkyl, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, and substituted derivatives of these radicals such that the monomer is unsymmetrical about the alkenic double bond, to form a carbanion which is in the form of either a dicerbanion salt having the dimeric structure



or a dicarbanion salt having the tetrameric structure



and subsequently reducing the carbanion, whereby a polymer is formed containing predominantly repeating units of the structure.



35 Electron transfer agents which are particularly effective in the formation of the carbanion are alkali metals, especially sodium. Suitable salts, M^+A^- , include sodium naphthalene and sodium diphenyl. The conditions under which the carbanion may be formed vary according to which monomer is used and depend upon either the thermodynamics or the kinetics of the particular system. Suitable conditions are, typically, direct reaction of the electron-transfer agent with a dilute solution of the monomer in 40 an inert solvent and under an inert atmosphere or in high vacuum.

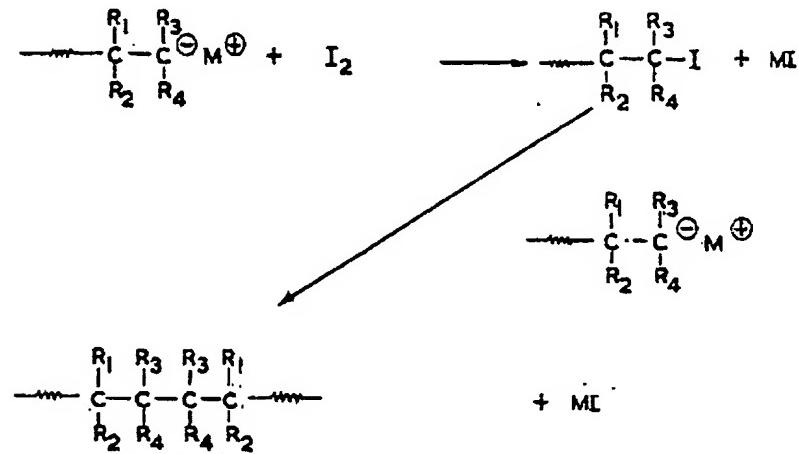
In general, the more reactive the electron-transfer agent the more likely is the 45 formation of the tetrameric carbanion. Thus, for example, a 'mirror' of sodium will normally give the dimer, whereas sodium/potassium alloy, in which the major reacting constituent is the very reactive potassium, yields the tetramer.

Where the electron transfer agent is a salt M^+A^- it is normally preferable to use it diluted with the same solvent as used for the monomer. Care must be taken to ex-

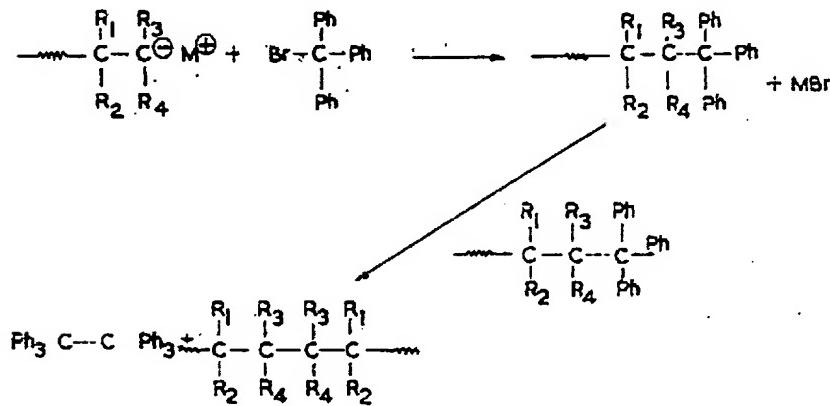
clude impurities such as water, oxygen and grease which could lead to premature termination of the carbanion chain. The most suitable conditions for the preparation of the carbanion may be determined readily by experiment, the formation of a carbanion being indicated unmistakably by its intense colour in solution.

Amongst available inert solvents, cyclic ethers such as tetrahydrofuran and dioxan have been found to be particularly useful. Alternatively other ethers such as dimethoxyethane may be used.

The preferred procedure for reducing the stable carbanion is to react the carbanion with a halogen such as iodine. Considering for clarity only one end of the carbanion, the reduction where M is an alkali metal for example takes place by the following reaction.



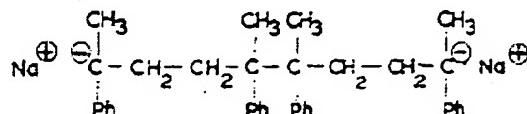
Reduction of the carbanion may of course be achieved by alternative procedures. These include electrolytic reduction of the carbanion and reaction with sterically hindered alkyl halides such as triphenylmethylbromide. The latter procedure is believed to proceed mainly by the following route.



Novel polymers may be prepared in accordance with the invention from a wide variety of olefinic monomers, especially vinyl monomers, which are unsymmetrical about the olefinic double bond. Such monomers include styrene, α -methylstyrenes, α -methyl- β -alkylstyrenes, β -methylstyrene, 3-chlorostyrene, vinyl pyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, and 4-vinylidiphenyl.

Typical examples of the preparation of polymers in accordance with the invention will now be described.

EXAMPLE 1
 α -methylstyrene monomer, thoroughly dried by refluxing with calcium hydride with periodic freezing and degassing, is dissolved in tetrahydrofuran to give a 0.5M solution. This solution is contacted at 0°C *in vacuo* with a sodium mirror (prepared by melting pure dry sodium *in vacuo*) on the wall of an evacuated flask. The intense red colouration of the tetrameric dicarbanion salt



is produced immediately. The solution is maintained in contact with the sodium mirror for 4 to 5 hours and then reacted *in vacuo* with pure dry iodine. Iodine in tetrahydrofuran solution is added slowly and carefully with vigorous mixing until the red colouration of the dicarbanion salt is removed to give a substantially colourless solution. Methanol is then added to yield a white precipitate. This is filtered off, redissolved in tetrahydrofuran and re-precipitated a further twice. The product is finally dried at 50°C for 12 hours to give a predominantly head-to-head and tail-to-tail bonded poly(α -methyl-styrene).

10

EXAMPLE 2

Where an electron transfer agent M^-A^- is used it is preferably reacted with a solution of the monomer while itself in solution in the same solvent. An apparatus in which the reaction between a solution of an unsymmetrical substituted alkene and a solution of an electron transfer agent may be readily carried out will be described with reference to the drawing filed with the provisional specification accompanying application No. 14209/67.

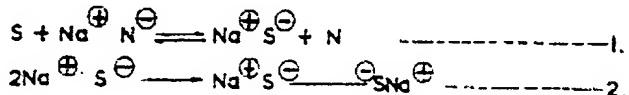
Reservoirs 1 and 2 contain respectively a solution of the monomer to be polymerised and a solution of electron transfer agent. The reservoirs are sealed from the remainder of the apparatus by conventional break seals each comprising a ferromagnetic rod 3 capable of being forcefully moved by an external magnetic field against a glass membrane 4 so as to break this membrane and release the contents of each reservoir into corresponding flasks 5 and 6.

In order to carry out a head-to-head polymerisation the apparatus is first evacuated by the vacuum pump with stopcocks 7, 9, 10 and 11 open and stopcocks 8 and 12 closed. When a good vacuum is established stopcock 7 is closed and the break seals sealing reservoirs 1 and 2 are broken to release monomer and catalyst respectively into flasks 5 and 6. Stopcock 11 is then closed and nitrogen is released into the apparatus from the supply 13 by opening stopcock 8 until a nitrogen pressure of about two-thirds of an atmosphere is achieved. This nitrogen pressure forces the monomer and electron transfer agent solutions through tubes 14 and 15 respectively from which they emerge into reaction vessel 16. The jets 17 and 18 are arranged so that the solutions meet and intermix very rapidly above a convex surface 19 which projects into the reaction vessel 16. The reaction product from reaction vessel 16, drains from the reaction vessel down tube 20 into collection vessel 21. The reaction may be stopped at any desired time by opening stopcock 11 to equalise the nitrogen pressure throughout the apparatus.

The collection vessel 21 may be sealed and removed at 22 and reaction product stored in this way is stable for some time. The preparation of the head-to-head linked polymer is completed by reducing the reaction product in vessel 21 with an appropriate agent such as a halogen solution which can be represented as being introduced from a reservoir 23 by opening stopcock 12. Mixing in vessel 21 may be achieved by means of a magnetically-operated stirrer 24. The resulting polymer may be isolated and purified in a conventional manner.

A typical preparation of a predominantly head-to-head linked polystyrene may be carried in the apparatus hereinbefore described as follows.

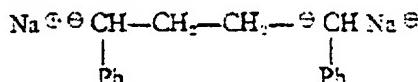
Firstly, an electron transfer agent, sodium naphthalene is prepared by reacting a solution of naphthalene in tetrahydrofuran with sodium *in vacuo*. The resulting tetrahydrofuran solution of sodium naphthalene is transferred to the polymerisation apparatus and reacted with a solution of styrene monomer in tetrahydrofuran. Reaction takes to form the stable dicarbanion according to the following equations (wherein S and N represent styrene and naphthalene respectively).



Reaction 2. is made to predominate over the normal stepwise polymerisation of styrene by ensuring that a large excess of electron transfer agent is present, thus re-

BEST AVAILABLE COPY

ducing the amount of free monomer in the system. The proportion of electron transfer agent should be at least five times that of the monomer to produce the dimeric dicarbanion salt, which has the structure



5 The dimeric dicarbanion salt is finally reduced by reaction with a solution of iodine in tetrahydrofuran until the characteristic colour of the dicarbanion is removed. The polymer is then precipitated by the addition of methanol, filtered off, re-dissolved in tetrahydrofuran and re-precipitated a further twice. After drying at 50°C for about 10 hours the product is found to be predominantly head-to-head and tail-to-tail linked polystyrene.

5

EXAMPLE 3

A stable carbanion salt of α -methyl-styrene in tetrahydrofuran is prepared as in Example 1 and titrated with triphenylmethyli bromide until a colourless solution is obtained. The resulting polymer is isolated and purified as in Example 1 and found to be predominantly head-to-head and tail-to-tail linked poly(α -methyl-styrene).

15

Certain sterically-hindered monomers such as 1,1-diphenylethylene are difficult to polymerise by the preferred process in accordance with the invention and are better prepared by rapidly treating the stable carbanion with sufficient excess halogen, preferably iodine to form the carbanion α,ω -dihalide and reacting this dihalide with a substantially equimolar quantity of further carbanion to yield a head-to-head and tail-to-tail linked polymer.

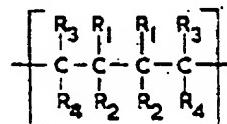
20

WHAT WE CLAIM IS:—

1. A process for the production of a head-to-head and tail-to-tail linked polymer consisting predominantly of repeating units having the structural formula

25

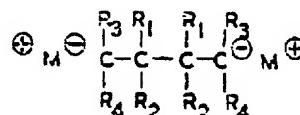
25



30

30

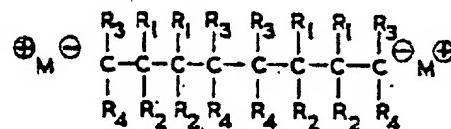
wherein R_1 , R_2 , R_3 and R_4 are hydrogen, halogen, or univalent radicals selected from the group comprising alkyl, aryl, aralkyl, alkoxy, aryloxy, alkoxy carbonyl, aryloxy carbonyl radicals and substituted derivatives thereof, which process comprises reacting an unsymmetrical substituted alkene which has the formula $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$ wherein R_1 , R_2 , R_3 and R_4 are as hereinbefore defined, with an electron transfer agent M or M^+A^- where M is an alkali metal or alkaline earth metal and A^- is an anion derived from a polynuclear aromatic hydrocarbon, to form a dicarbanion salt having either the dimeric structure



35

35

or the tetrameric structure

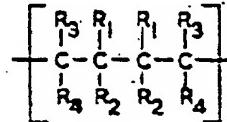


and subsequently reducing the dicarbanion salt with a halogen to yield the polymer.

2. A process for the production of a head-to-head and tail-to-tail linked polymer consisting predominantly of repeating units having the structural formula

40

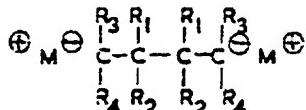
40



5

wherein R₁, R₂, R₃ and R₄ are hydrogen, halogen, or univalent radicals selected from the group comprising alkyl, aryl, aralkyl, alkoxy, aryloxy, alkoxy carbonyl, aryloxy carbonyl radicals and substituted derivatives thereof, which process comprises reacting an unsymmetrical substituted alkene which has the formula R₁ R₂ C=C R₃ R₄ wherein R₁, R₂, R₃ and R₄ are as hereinbefore defined, with an electron transfer agent M or M⁺A⁻ where M is an alkali metal or alkaline earth metal and A⁻ is an anion derived from a polynuclear aromatic hydrocarbon, to form a dicarbanion salt having either the dimeric structure

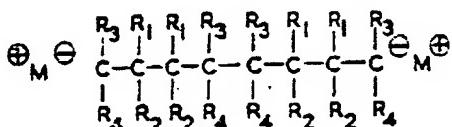
5



10

or the tetrameric structure

10

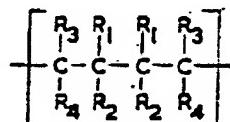


and subsequently reducing the dicarbanion salt electrolytically to yield the polymer.

3. A process for the production of a head-to-head and tail-to-tail linked polymer consisting predominantly of repeating units having the structural formula

15

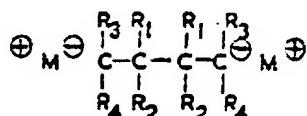
15



20

20

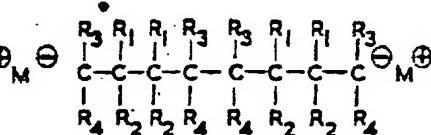
wherein R₁, R₂, R₃ and R₄ are hydrogen, halogen or univalent radicals selected from the group comprising alkyl, aryl, aralkyl, alkoxy, aryloxy, alkoxy carbonyl, aryloxy carbonyl radicals and substituted derivatives thereof, which process comprises reacting an unsymmetrical substituted alkene which has the formula R₁ R₂ C=C R₃ R₄ wherein R₁, R₂, R₃ and R₄ are as hereinbefore defined, with an electron transfer agent M or M⁺A⁻ where M is an alkali metal or alkaline earth metal and A⁻ is an anion derived from a polynuclear aromatic hydrocarbon to form a dicarbanion salt having either the dimeric structure



25

25

or the tetrameric structure



and subsequently reducing the dicarbanion salt with a sterically hindered alkyl halide to yield the polymer.

4. A process according to claim 1 in which the halogen is iodine.

30

30

5. A process according to any preceding claim in which the electron transfer agent is sodium.

6. A process according to any one of claims 1-4 in which the electron transfer agent is a sodium/potassium alloy.

35

35

7. A process according to any one of claims 1-4 in which the electron agent is sodium naphthalene or sodium diphenyl.

8. A process for the production of a head-to-head and tail-to-tail linked polymer substantially as hereinbefore described in Examples 1, 2 or 3.

9. A polymer containing predominantly head-to-head and tail-to-tail repeating monomer units when produced by a process according to any preceding claim.

10. Poly (α -methylstyrene) containing a predominance of head-to-head and tail-to-tail repeating units of α -methylstyrene.

5 11. Polystyrene containing a predominance of head-to-head and tail-to-tail repeating units of styrene.

J. V. GOODFELLOW,
Chartered Patent Agent.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

BEST AVAILABLE COPY